Spin-Phonon coupling in Y_2NiMnO_6 double perovskite probed by Raman spectroscopy

Raimundo Bezerra Macedo Filho

Departamento de Física, Universidade Federal do Ceará, Fortaleza - CE, Brazil and

Departamento de Física, Instituto Federal De Educação,

Ciência E Tecnológia do Maranhão,

65030-005, IFMA, São Luís - MA, Brazil

Alejandro Pedro Ayala

Departamento de Física, Universidade Federal do Ceará,

Campus do Pici, 60455-760, Fortaleza - CE, Brazil

Carlos William de Araujo Paschoal*

Departamento de Física, CCET, Universidade Federal do Maranhão,

65085-580, São Luís - MA, Brazil and

Department of Materials Science and Engineering,

University of California Berkeley, 94720-1760, Berkeley - CA, United States[†]

Abstract

We performed Raman spectroscopy measurements under temperature changes from 10 K up to 850 K to probe the phonon-spin coupling in Y_2NiMnO_6. The spin-phonon coupling was observed as a softening of the stretching mode, indicating this phonon stabilizes the magnetic interaction. The result indicates the rare earth ionic radius in Re_2NiMnO_6 double perovskites is not the unique parameter influencing the spin-coupling magnitude.

[*] Author whose correspondence should be addressed: Phone +55 98 3301.9209; Fax: +55 98 3301 8204

[†] paschoal@ufma.br; paschoal.william@berkeley.edu; paschoal.william@gmail.com

Recently, multiferroic oxides have attracted much attention due to their possible applications as more efficient memories [1] and spintronics [2]; additionally they show unique fundamental physics properties [3], mainly as thin films [4–6]. In this scenario, perovskite-based materials, such as $BiFeO_3$ and $YMnO_3$, play an essential role as a model for most of the multiferroic compounds [7].

Many ordered double perovskites $RE_2Me^{2+}Mn^{4+}O_6$ (with RE = rare earth and Me = Metal) are ferromagnetic due to the $Me^{2+}-O-Mn^{4+}$ superexchange interaction, and they can exhibits several other interesting properties such as large magnetocapacitance and magnetoresistance [8], relaxor ferroelectricity [9]. Quantum mechanical calculations also have showed a multiferroic character in some of members of this family [10].

Particularly, in the case of the double perovskite Y_2NiMnO_6 (YNMO), recent density-functional theory (DFT) calculations [11] were performed to elucidate the possibility of finding novel multiferroics in rare-earths RE_2NiMnO_6 double perovskites. This investigation proposed YNMO as polar in its magnetic ground state with an intrinsic polarization comparable with other magnetically driven ferroelectrics [12–15]. In this case, YNMO has an E^*-type ferromagnetic state which is well known to assist the ferroelectricity. It was observed a giant dielectric tunability in bulk YNMO at approximately room temperature, which was attributed to the charge ordering of Ni^{2+} and Mn^{4+} ions [16]. Also, Maiti $et\ al$ [17] showed, using Rietveld analysis of the X-ray powder diffraction data of YNMO nanoparticles obtained by a sol-gel method, it has a monoclinic structure. Using XPS studies it was observed that a Mn^{3+}/Mn^{4+} ratio of 0.64 in the nanocrystals. The temperature variation of resistivity was explained on the basis of small polaron hopping conduction mechanism, being Mn^{3+} and Mn^{4+} at the hopping sites. The nanocrystals exhibited ferromagnetic properties with a Curie temperature around 92 K. This behaviour was ascribed to a ferromagnetic superexchange interaction between Mn^{4+} and Ni^{2+} ions. Spin glass behavior was ruled out on the basis of ac magnetic susceptibility data. The nanocrystals exhibited a peak in the dielectric constant at a temperature of 535 K indicating a ferroelectric transition. This is consistent with the recent theoretical prediction made on the basis on DFT calculations.

Ferromagnetic compounds usually exhibit a spin-phonon coupling and Raman spectroscopy has been extensively employed to study this effect in several perovskites [18–26], including double perovskites [18–26]. Thus, the aim of this contribution is to use Raman spectroscopy to probe the spin-phonon coupling in YNMO ceramics.

YNMO was synthesized by a solid state route according to a stoichiometric mixture of Y_2O_3, NiO and MnO. The sample was calcined ten times at 1000 ^{o}C for 12h. Between each calcination the sample was grounded in an agatha mortar and sieved to obtain a homogeneous powder. Finally, the sample was sintered at 1400 ^{o}C for 24h. The crystalline structure was investigated with X-ray powder diffraction (XRD$-$Bruker D8 Advance), in a continuous scanning mode using Cu-Kα radiation. The XRD pattern was compared with data obtained by Tang et al [16], which confirms the YNMO phase obtention. Also, the diffraction pattern indicates a small quantity of Y_2O_3 ($< 4\%$) as a residual phase. This secondary phase is usual in the synthesis [25].

Raman spectroscopy measurements were performed in a Jobin-Yvon T64000 Triple Spectrometer configured in a backscattered geometry. The 514.5 nm line of an Innova Coherent laser operating at 200 mW, focused on the sample by a long-working distance objective (20x, 20.5 mm), was used to excite the signal that was collected in a N_2-cooled CCD system. Low temperature measurements were performed by using a closed-cycle He cryostat where the temperature was controlled within 0.1 K. High temperature measurements were performed in a homemade furnace controlled by a PID temperature controller with accuracy of 1 K.

The Raman spectrum recorded at $T = 20$ K is shown in Figure 1. The most intense Raman mode of Y_2O_3 at around 377 cm^{-1} [27, 28] was not observed, confirming the low concentration of secondary phase. We have observed 13 first-order Raman actives modes at low temperatures. This is the largest number of modes observed for a RE_2NiMnO_6 double perovskite. As early works showed, no structural phase transitions were observed in this perovskite below room temperature. Thus, at 20 K we expected the crystalline structure of YNMO to remain in the room temperature monoclonic structure with space group $P2_1/n$. In this structure, rare earth and all oxygens occupy general positions into $4e$ Wyckoff sites, while Ni and Mn ions occupy $2c$ and $2b$ Wyckoff sites.

In general, low symmetry structures of ordered double pervoskites are a consequence of small distortions of the cubic $Fm\bar{3}m$ arystotipe lattice. It was also noted that the vibrational spectra is determined by the oxygen octahedra around the higher valence cation [29]. Based on this model, the 24 Raman active optical modes expected for this structure are distributed according the irreducible representation of the $2/m$ point group as follows: $6T(3A_g+3B_g)+ 6(3A_g + 3B_g) + 2\nu_1(A_g + B_g) + 4\nu_2(2A_g + 2B_g) + 6\nu_5(3A_g + 3B_g)$, where lattice modes (translational, T, and librational, L) and oxygen octahedron internal are expected below

and above 380 cm^{-1}, respectively. Semiempirical calculation performed by Illiev et al [30] in a isostructural Mn-based double perovskite suggest that symmetric (ν_1) and antisymmetric (ν_2) modes internal of the oxygen octahedron should be observed around 652 cm^{-1} and 420 cm^{-1}, whereas the octharon deformation (ν_5) is expected around 420 cm^{-1}. Following the proposed symmetry reduction 2, 6 and 4 bands related to the ν_1, ν_5 and ν_2 modes should be expected in very good agreement with the experimental results. Furthermore, polarized Raman spectra recorded by Iliev et al. [30] on La$_2$CoMnO$_6$ show that the ν_1 mode with B_g symmetry is weaker than the one belonging to the A_g representation, as observed in our Raman spectra (Figure 1). Notice that in our results Raman bands are much more splitted than in La$_2$CoMnO$_6$, this effect can be ascribed to the strongest monoclinic deformation of YNMO when compared to La$_2$CoMnO$_6$ [31].
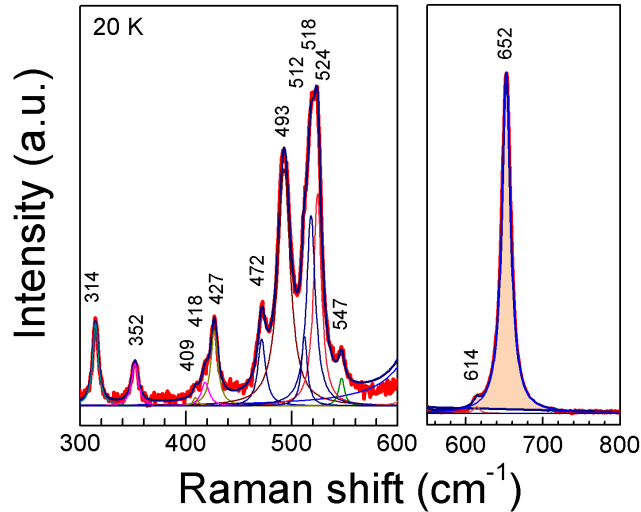

FIG. 1. Raman spectrum of Y$_2$NiMnO$_6$ double perovskite observed at 20 K.

Figure 2 shows the temperature-dependent Raman spectra obtained for YNMO in the temperature range from 20 K up to 850 K. As it can be observed, there are not remarkable changes in the spectra as it is usually observed in double perovskites [26, 32? –34].

To investigate the spin-phonon coupling in YNMO, we have analyzed the temperature dependence of the wavenumber of the main observed phonons. Figure 3 shows the temperature evolution of two of the most representative bands of the YNMO Raman spectra. In the absence of structural phase transitions, the main contribution to the temperature dependence of the phonon wavenumber is expected to be the anharmonicity, as proposed by
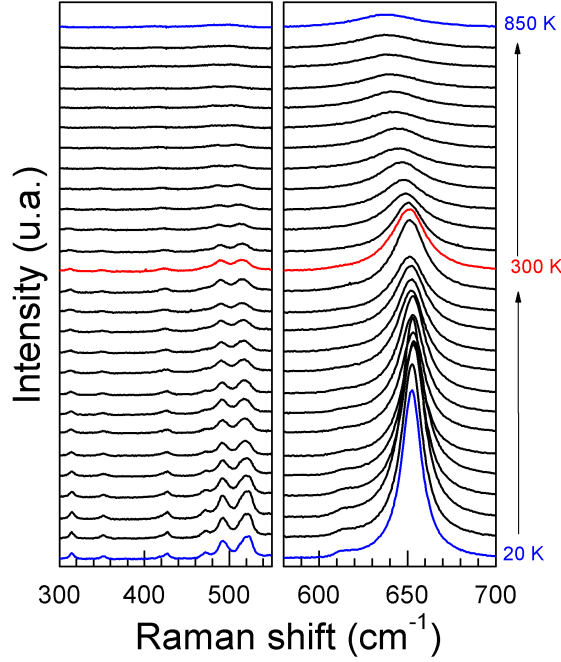
FIG. 2. Temperature-Dependent Raman spectra of Y_2NiMnO_6 double perovskite.

Balkanski [35]. In this model, the energy of the phonon can be described by the following expression: $\omega(T) = \omega_o - C\left(1 + \frac{2}{e^{\hbar\omega_o/kT}-1}\right)$, where C and ω_o are adjustable parameters. However, in several perovskites it was observed that the magnetic order induces a renormalization of the phonon frequencies, which is proportional to the spin correlation function [36]. Within the mean-field approximation, the phonon renormalization frequency is proportional to $(M(T)/M_o)^2$, where $M(T)$ and M_o are the magnetization at temperatures T and 0, respectively. Figure 3 shows the temperature evolution of two of the most representative bands of the YNMO Raman spectra. The phonon observed at 493 cm^{-1} at 20 K exhibits the usual temperature dependence governed by the anharmonic phonon-phonon scattering in the whole range of investigated temperatures. On the other hand, the most intense band of the YNMO Raman spectra (650 cm^{-1} at 20K) exhibits the typical deviation in the temperature-dependence ascribed to the spin-phonon coupling in several double perovskites [30, 37, 38].

The temperature dependence of the departure from the anharmonic behavior of the most intense Raman band is plotted in figure 4. In the same figure, it is also shown the square of
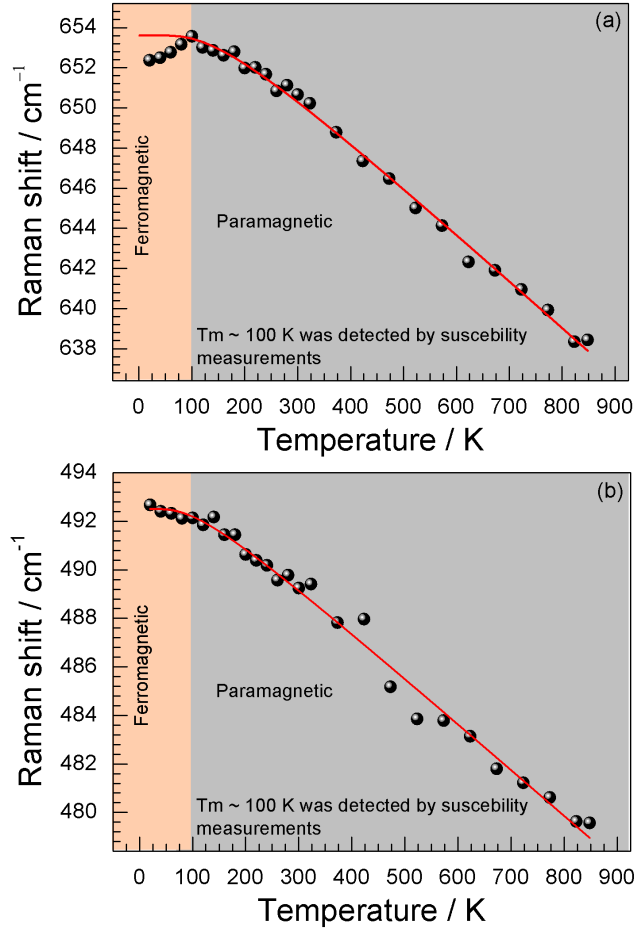
FIG. 3. Temperature dependence of the phonon positions of two typical modes observed for YNMO.

the magnetization extracted from Maiti *et al.* [17]. The comparison of these curves confirms that the phonon renormalization scales are well within the square of the magnetization as predicted by the mean field theory [36]. A similar behavior was observed in several double perovskites confirming the spin-phonon coupling in YNMO.

At this point it is important to emphasize that our results do not agree with the model proposed by Bahoosh *et al.* [39]. These authors suggested an A-site ferroelectric transition driven by A-site cations, as it was observed in Bi-based multiferroic systems. The existence of a spin-phonon coupling, as proven in this contribution, is in good agreement with the model proposed by Kumar *et al.* that based on DFT calculations, suggested the ferroelectric transition is driven by all ionic displacements, with the largest ones associated to oxygen and nickel ions [10]. In this case, the softening of the stretching phonon indicates this phonon is
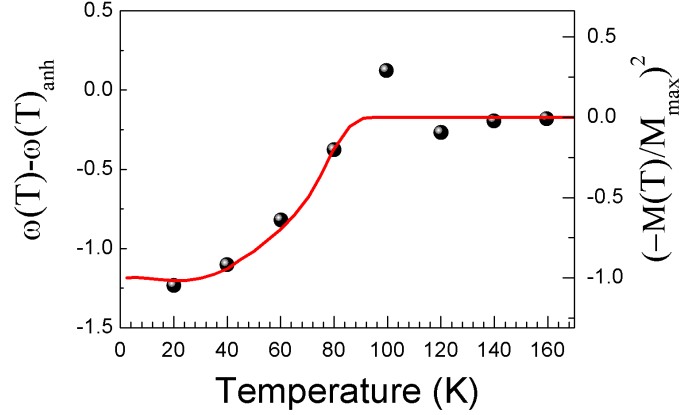
FIG. 4. Temperature dependence of the departure from the anharmonic behavior of the most intense Raman band (650 cm^{-1}) compared with $M^2(T)/M^2_{max}$ (taken from ref. [17]).

stabilizing the magnetic phase. In addition, Nair *et al* [40] proposed that the size of the RE ion is correlated to the strength of spin-phonon coupling. In that case, that the RE ionic radius decreasing should give rise to the reduction of the spin-phonon coupling, once the observed spin-phonon coupling in Tb$_2$NiMnO$_6$ is weaker than those observed in La$_2$NiMnO$_6$ and Pr$_2$NiMnO$_6$.[40] However, the strong spin-phonon coupling reported in YNMO, suggests that the RE ionic size is not the unique parameter determining the spin-phonon coupling, since this effect is observed in YNMO although the Y ionic radii is smaller than the one of Tb.

Summarizing, in this work we investigated the temperature-dependent Raman spectra of Y$_2$NiMnO$_6$ double perovskite between 20 K and 850 K. We showed there is a spin-coupling indicating the ferromagnetic transition undergone by this material at around 100 K. No remarkable spectral changes ascribed to structural phase transitions were observed in the investigated temperature range. However, the temperature dependence of the symmetric stretching of the oxygen octahedra exhibits an anomalous softening below the ferromagnetic transition, which can be related to the phonon renomalization induced by the spin-phonon coupling.

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